High Performance Materials by the Powder Particle Assemblage

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Abstract

The techniques of the particle assemblage have been developed to create intelligent materials by assembling particles. The particle assemblage techniques of particle arrangement, probe manipulation and composition are introduced in this paper. The probe manipulation is carried out in the air under optical microscopic observation and in vacuum under the SEM observation. We can fabricate 3-dimensional structures as designed from fine particles to some extent. Photonic crystals and ceramics heaters are fabricated by the probe manipulation in SEM and by the composition, respectively.

1. Introduction

Both the weight and capacity of portable phone are decreased one-tenth for 10 years. The performance is greatly improved simultaneously with the lightening and miniaturization. Similar miniaturization is requested for almost products, especially for the machines and tools used in the information technology.

Further miniaturization will be attained not only by the further integration but also new materials. The materials must have the functions of the electronic circuit and/or mechanical parts. The materials must have multi-functions. Science and Technology Agency urged researchers to develop intelligent materials since 1989[1]. The intelligent materials are just used for the above purpose.

We proposed that new functional materials and/or multi-functional materials can be assembled from particles and that the particle assemblage is one of the ways to create intelligent materials at the second International Conference of Intelligent Materials held in 1994[2]. Since then, we have developed new techniques of particle assemblage.

Assembling methods of fine particles are classified into two from the number of particles treated. One is to assemble a particle one by one, and the other is assemble mass of particles at a time. We developed a probe manipulation method[3,4], which assembles a particle one by one, and a beam arranging method[5], which assembles mass of particles at a time. Besides them, a method to prepare composite particles is developed for the particle assemblage[6].

As a result of the research on the particle assemblage, we can fabricate two-dimensional patterns and three-dimensional structures from fine particles to some extent. The three methods developed for the particle assemblage and two examples of the applications of the techniques, photonic crystals and flexible sheet heaters, are introduced in this paper.

2. Assembling Techniques of Fine Particles

2.1Probe Manipulation

Several tools are proposed to manipulate fine particles one by one, for example, probe type, tweezers or chopstick type[7], capillary type[8], dipole electrode type[9] etc. Probe has the simplest structure among them.

Two kinds of apparatus are made for the probe manipulation of fine particles. One manipulates under the optical microscopic observation and the other manipulates under the SEM (scanning electron microscope) observation. The general characteristic of each manipulator is compared in Table 1.

The apparatus and manipulation method under the SEM observation is described in 3.1. Thus the detail of the other apparatus and method is explained in this section.

The special feature of our apparatus equipping with the optical microscopes is its function. Ordinary manipulators pick up an object, carry and place it at a desired position. Our manipulator has a welding function, i.e.; metal particles can be welded after placing them on a metal substrate.

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Table 1 General characteristic of two manipulators of probe type

	Observation	Particle size	Atmosphere	Dominant force
1	optical microscope	above 10 µm	Air	Gravitation Electrostatic force
2	SEM	above 100 nm	Vacuum	Electrostatic force Intermolecular force

Our apparatus is developed to manipulate fine particles on a metal substrate using a tungsten probe. Gold plate or thin gold film pasted on an ITO glass is used for the substrate. The tungsten probe is available in a market.

A power source is installed in the manipulator, and desired voltage is applied between the probe and the substrate. The output voltage is variable from 0 to 10kV at a step of 100V.

The manipulation is carried out as follows. Keeping the tip of probe with the top of the particle, 10-50V is applied between the probe and substrate. As the particle is adhered at the probe, the probe picks up the particle, moves and put it at the desired point on the substrate.

When the particle is placed, the probe is in contact with the particle. Applied voltage is increased to 10kV for several seconds in that condition. Glow discharge is observed between the particle and the substrate, and the particle is welded at the substrate. Tough bonding strength is obtained by the non-contact welding following the above contact welding. The non-contact welding is done by pulling up the probe about 50 µm and applying 2kV to generate glow discharge for several seconds.

Figure 1 shows the example of 3-dimensinal microstructure composed of gold particles of 40-50 µm. The characters vertically stand on the gold substrate.

Fig.1 Characters "N", "R", "I" and "M" composed of gold particles

2.2 Beam Arrangement

The beam arrangement is a method to deposit particles at desired positions at a time.
In contrast with the probe manipulation, a large number of particles are placed by one process in the beam arrangement.

The basic idea is to prepare the preferential seats for the particles on the substrate. We make negative or positive electrification patterns by irradiating electrons or ions on an insulating substrate. The particles will preferentially settle down on the patterns by the electrostatic force.

Dual beam apparatus (Seiko Instrument, SMD7000) shown in Fig. 2 is used to draw the electrification patterns. It is equipped with both electron beam gun and Ga ion beam gun. A polished insulating substrate is placed in the vacuum chamber. When the electrification patterns are drawn, the substrate is tilted perpendicular to the beam and the computer controls the irradiation area and dose.

The substrate is immersed in a solution, where fine particles are suspended. The particles are attracted to the

electrification pattern by the electrostatic force[10]. Keeping the substrate in a suspension for a few minutes, enough number of particles is adhered and makes particle patterns. The substrate is pulled up and dried in an air after washing with the volatile solvent.

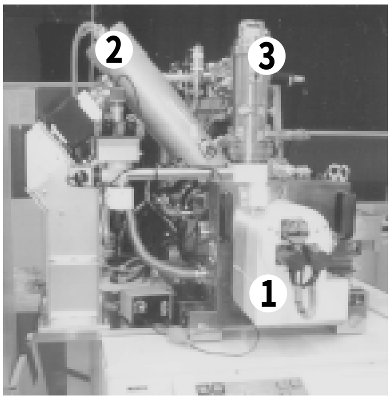

Fig. 2 Apparatus for drawing the electrification patterns
1: chamber, 2: ion beam gun and 3: electron beam gun

The examples of particle pattern are shown in Fig. 3. Silica particles of 5 µm are lined to form a circle pattern as shown in Fig. (a). If the electrification spots are formed on the substrate, only one particle can be put on each spot as shown in Fig. (b).

This method is a margin to improve the arranging results. The method to line particles is applicable to make circuits or to repair circuits. The method to put one particle at each spot is applicable to make sensor array.

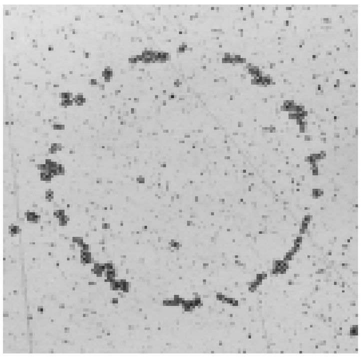

Fig.3 Silica particles of 5 µm on a circle pattern

2.3 Composite Particle

Composite particles are raw materials of high performance materials created by the particle assemblage. The composite particles are prepared by arranging child particle on the surface of core particles. The method is, therefore, also one of the particle assemblage techniques.

We developed a novel method to prepare composite particles called forced electrification method[11]. The process is as follows. Core particles are charged into a metallic vessel. The core particles are electrified positively by applying positive high voltage to the vessel. The child particles are electrified negatively by the same way. Mixing both the particles, composite particles are produced. Because the positive core particles and negative child particles attract each other by the Coulomb's force.

The child particles with the same electric charges repel each other. The child particles, therefore, does not touch to the other child particle on the surface of core particle. In other words, child particles are dispersed and electrically isolated. This is a key to apply the composite particles.

We make a flexible PTC sheet composed of composite particles prepared by the forced electrification method. The

details of the application is described the following section. The important point is that the child particles are electrically isolated.

3. Application of the Particle Assemblage

3.1 Photonic Crystal

Materials, which have a periodic structure of refractive index and the periodicity is comparable to the wavelength of light, are called photonic crystal. Just as electrons form band structures in the crystal, so photons form band structures in the photonic crystal.

Photons in the photonic crystal show unique behavior due to the band structures[12]. The photonic crystal is, therefore, expected to be a new material for optical devices. Following the theoretical studies, many researchers try to fabricate the photonic crystal.

Two major approaches are researched, i.e., lithographic techniques and colloidal techniques. They have both merits and demerits. The former has advantages in the quality of the products and the latter in the productivity. We demonstrated the third approach of the particle assemblage.

Sub-micron sized particles are arranged by the probe manipulation in FE-SEM. The probe is a glass fiber coated with gold, and is manipulated with a joystick under the SEM observation. The operator measures the size of the particle aided by computer, picks only the particles of the same size, and places them at the predetermined position.

The particle size is comparable to the wavelength of visible light. Since the intermolecular force is dominant for such the small particles, the particles can be picked up and deposited only by maneuvering the probe[13]. Furthermore, the structure is tough enough without bonding treatment. Figure 4 shows the product composed of 2 μm polyvinyltoluene spheres.

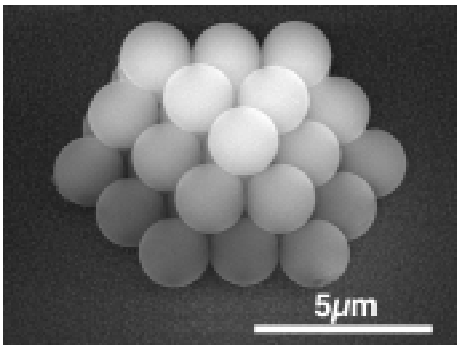

Fig. 4 Photonic crystal fabricated by manipulator in SEM

The most important feature of this method is that completely defined photonic crystal can be fabricated. It means that both the photonic crystals without defects and with defects at the desired position can be fabricated. Diamond structure, which is important in the practical use, can be obtained[14]. On the other hand, only the close packed structures are obtained by the colloidal method.

The probe manipulation method is effective for the experimental study of the photonic crystal. For example, one of the authors experimentally showed the variation of the photonic bands formed in the 2-dimensional close packed crystal with the constituent number of particles[15].

3.2 Flexible Sheet Heater

Semiconducting $BaTiO_3$ is a representative PTCR (positive temperature coefficient of resistivity) material. As the temperature is increased, the resistance steeply increases about five or six orders of magnitude near the Curie point.

According to its unique temperature dependence of the resistance, it is used to heaters, which temperature are self-controllable, and protective devices, which limit the current against overheating. They are employed to a practical use like small parts of home electronic appliances. However, they are not used to large heaters such as floor heating system, owing to their brittleness.

If we can compensate the defect of brittleness, they are more useful materials. Composite particles are one of the ways to solve the problem. Composite particles of semiconducting $BaTiO_3$ of 650-700 μm and In of -20 μm are prepared by the forced electrification method. It is reported that the PTCR property of packed bed of the composite particles is almost the same with that of the sintered disk of $BaTiO_3$[16].

Thus the sheet, where the composite particles are sandwiched between two thin electrodes, will show PTCR property. It will be not brittle but flexible, because the composite particles are only packed and the external stress is relaxed by the displacement of relative locations of composite particles.

Figure 5 shows the appearance and the structure of the trial sheet heater. The composite particles are charged inside the insulating frame, which is placed between the aluminum foil electrodes. The heater is inserted in a heat resistant and airtight plastic bag. Lead wires are passed out through the holes on the bag, and the holes are sealed by an adhesive agent. The bag is sealed by heat after evacuation[17].

The compression by the atmospheric pressure fixes the relative location of the composite particles and the electrodes. The size of the trial sheet heater is 20x20 mm and the thickness is less than 2mm. It shows PTCR property and is flexible as is expected.

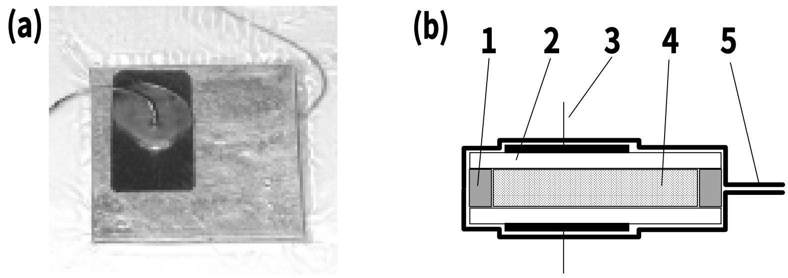

Fig. 5 Appearance of trial sheet heater(a) and its cross section(b)
1: insulating frame, 2:electrode, 3: lead wire, 4: composite particles and 5: air-tight bag

4. Conclusion

The concept of the particle assemblage is to create new functional materials by integrating various particles. The novel techniques to manipulate and arrange fine particles have been developed for the particle assemblage in our research group. The probe manipulation method, beam arrangement method, and preparation method of composite particles are introduced.

Photonic crystal is fabricated by the probe manipulation in SEM, and flexible sheet heater is made from the composite particles of $BaTiO_3$ and In.

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